INFLUENCE OF MATRIX DENSIFICATION UPON STRUCTURE AND ELASTIC PROPERTIES OF CARBON-CARBON COMPOSITE SHELLS

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Carbonisation of "green" composite shells reinforced with carbon yarn braid and soaked with phenolic resin yielded carbon-carbon composite cylindrical shells. The obtained porous composite material was densified by impregnation with various precursors of secondary carbon matrix. By measuring the longitudinal and tangential elastic moduli of the composite shells by a resonant frequency technique their gradual stiffening was monitored. The roles of the braiding angle and of the processing parameters (heat treatment, densification, and impregnant type) upon constitution of the composite shell elasticity are discussed.

INTRODUCTION

Carbon fibre reinforced carbon (CFRC, carbon-carbon) composites address the need to toughen polycrystalline carbons or graphite, i.e. fundamentally brittle (but refractory) materials. They out-perform metals and ceramics in terms of specific strength and thermal capability even at the highest temperatures (in inert atmospheres or in vacuum) and are irreplaceable at certain space/rocket applications, aircraft brake production etc. [1]. Moreover, due to their biocompatibility they have a potential of application also in human surgery (bone plates, implants). Their manufacture routes consist of two basic steps: forming the fibrous substrate and densifying this with carbon matrix. The latter step involves either impregnating the substrate with a suitable carbon precursor (e.g., thermosetting resin or coal tar pitch) and its carbonisation (i.e., pyrolysis to 1000 °C) or a direct carbon deposition (e.g. pyrolytic carbon from gaseous phase).

The means of forming the fibres into a shape prior to densification are governed by the ultimate application. In majority of cases the woven reinforcement (fabric) is routinely used, particularly in applications subjected to planar loading. If more complex shapes are required, namely those with rotational symmetry, a braided reinforcement can be very useful though it cannot achieve as high a fibre volume fraction as filament winding. The interlaced nature of braids provides an enhanced level of structural integrity. The current trend is to expand to large-diameter braiding, multi-directional braiding (often computer-aided design and manufacturing) and interlocking 3D-braiding [2] in which the interlaminar properties are improved by diagonal yarns linking adjacent layers.

The CFRC shells can serve, e.g., as convenient substrates for zero-valent metals (Fe, Sn, Zn) for remediation of groundwaters contaminated by halogenated hydrocarbons [3]. The shell form of the CFRC is advantageous also in gas purification or filtering processes that are considered prospective. In the present study we have therefore investigated the carbon densification process of a simple composite structure reinforced with braided carbon yarns. For monitoring the material development we have combined non-destructive measurement of elastic properties, porosity determination, and microscopic structure investigation.

EXPERIMENTAL PART

Manufacture of the braided reinforcement

The braiding process is known for its simplicity: two or more yarn systems are intertwined in the bias direction at an angle less than 90° (figure 1). In our study we have employed a Dotex PSJ 64 braiding machine (manufactured by Dotex, Nový Jičín, Czech Republic). Maximum of 64 spool carriers together with (optional) 32 longitudinal yarns yielded a $0° \pm \theta$ braid (the braiding angle θ is half the angle of the interlacing between yarn systems). The optical micrograph of an outer surface of the braided structure is given in figure 2. For braiding the carbon yarns (Toray T800 6K from Soficar, France) some improvements of the braiding machine were necessary in order to cope with the fibre brittleness. They comprised design measures aimed to avoid bending of the yarns at small curvature radii and to maintain optimum yarn pre-stressing necessary for preventing formation of loops.

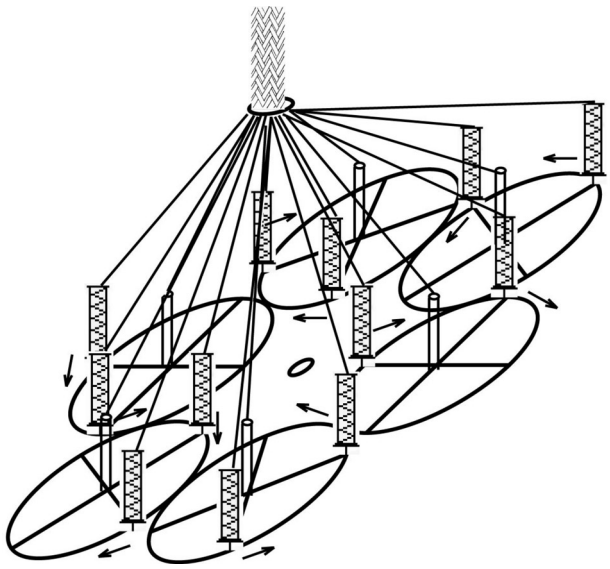


Figure 1. Principle of braiding.

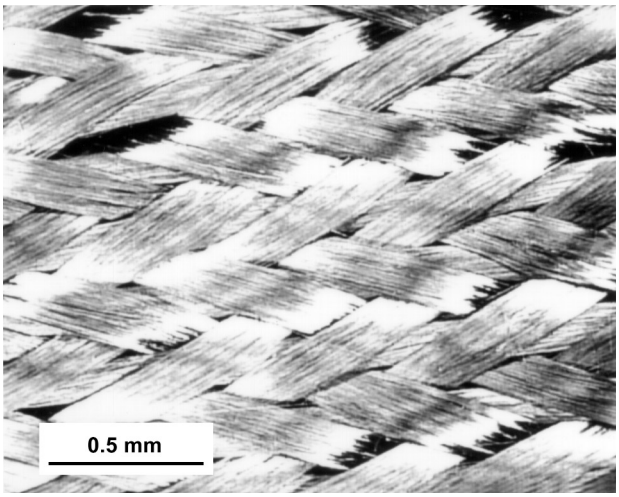


Figure 2. Optical micrograph of an outer surface of the braided structure.

The wall thickness of the braid can be increased by repeatedly braiding over the existing structure (layering). For composite shell making we have utilised a triple braid characterised by pick spacing 4.cm^{-1}, θ = 42 or 55° and wall thickness 2.5 mm. Its inner diameter (12 mm) was achieved by braiding over a cylindrical mandrel.

Composite manufacture

When making a primary ("green") composite shell the 150 mm piece of the braid was slid on a silicon hose with outer diameter of 14 mm and soaked with ethanol solution of phenolformaldehyde resin (Umaform LE made by Synpo, Czech Republic). This "prepreg" (impregnated preform) was in a heated cylindrical form (internal diameter 18 mm) pneumatically moulded by pressurising the hose to 2.5 MPa and cured at 120 °C for 2 hrs yielding thus a carbon braid reinforced polymer composite shell. In order to convert it into the CFRC shell the carbonisation to 1000 °C was carried out in a nitrogen atmosphere. During this manufacture step the resin matrix changed to a carbon one. Optical micrograph of the polished cross-section cut perpendicularly to the shell (z) axis is given in figure 3. Due to inevitable mass-loss of the resin matrix the carbonised shells contained a relatively small amount of carbon matrix and in order to reduce the void content and to improve the mechanical properties it was necessary to impregnate and re-carbonise them. The same phenolformaldehyde resin or a commercially available coal tar pitch (softening point 116.5 °C, product of DEZA, Czech Republic) were used as impregnants. For comparison sake, other shells were impregnated by pyrolytic carbon obtained from propane decomposition till approximately the same weight increments were achieved (table 1).

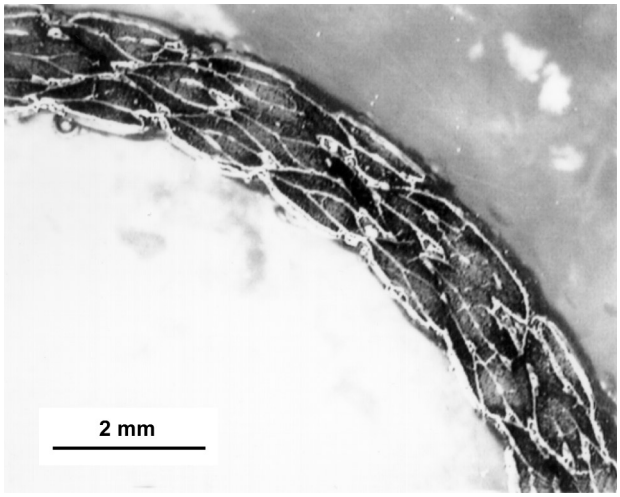


Figure 3 Optical micrograph of the polished cross-section cut perpendicularly to the shell (z) axis.

Monitoring the shell densification process

Porosity and elastic parameters

Open (i.e., accessible to water) porosity of the shells was measured by water penetration method after particular manufacture steps (table 1). At the same manufacture levels (i.e. G, C, CIC, and CICIC), mechanical properties of the shells were monitored by measuring two of their elastic constants (elasticity moduli E_{zz} and $E_{\phi\phi,}$ figure. 4) using a resonant frequency method. Resonant frequency tester Erudite (C.N.S. Electronics Ltd., UK) was used for the measurement. In this device, specimen vibrations are excited by electrodynamic forces. Frequency spectra were interpreted by an original procedure [4]. The latter

Table 1. Processing of the investigated shells.

	θ	G	C	CIC	CICIC
A1	42°	cured	carbonised	PyC infiltrated 36 hrs.	PyC infiltrated another 27 hrs.
B1	42°	cured	carbonised	resin impreg., recarbonised	2nd resin impreg., recarbonised
C1	42°	cured	carbonised	pitch impreg., recarbonised	2nd pitch impreg., recarbonised
A2	55°	cured	carbonised	PyC infiltrated 36 hrs.	PyC infiltrated another 27 hrs.
B2	55°	cured	carbonised	resin impreg., recarbonised	2nd resin impreg., recarbonised
C2	55°	cured	carbonised	pitch impreg., recarbonised	2nd pitch impreg., recarbonised

enabled to determine values of E_{zz} and $E_{\phi\phi}$ from resonant frequency spectrum of longitudinal vibrations if at least 3 resonant frequencies are detected and identified.

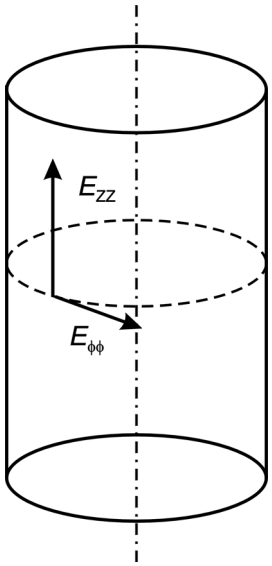


Figure 4. Longitudinal E_{zz} and tangential $E_{\phi\phi}$ modulus in cylindrical co-ordinates.

Microstructure

Microstructure of the CFRC shells was investigated by optical microscopy of their cross-sections mounted in transparent resin and polished by diamond paste. Anisotropy of carbon matrix was visualised when observed in a polarised light: while pyrolytic carbon and carbonised pitch reveal anisotropic regions of various extension and anisotropy degree, carbonised resin is almost isotropic. This phenomenon enabled to distinguish easily between different types of carbon matrix in the CFRC composite.

RESULTS AND DISCUSSION

Open porosity detected at particular manufacture levels for the carbonised shell specimens A2, B2, and C2 is plotted in figure 5 and a similar behaviour is revealed also by another specimen set (A1, B1, and C1). The mentioned porosity decrease is accompanied by

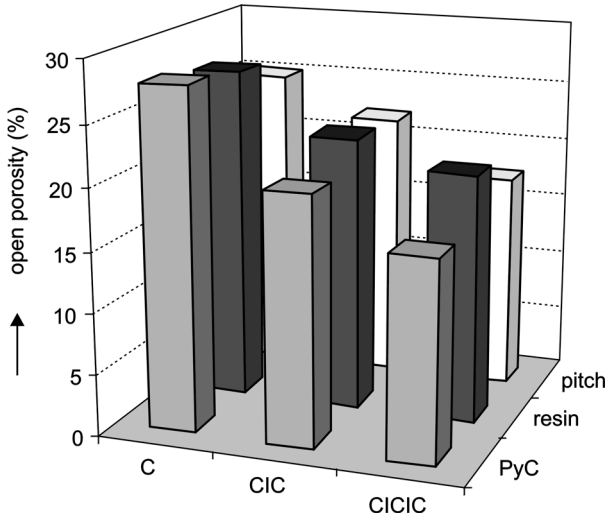


Figure 5. Open porosity at various manufacture levels for the shell specimens A2, B2 a C2.

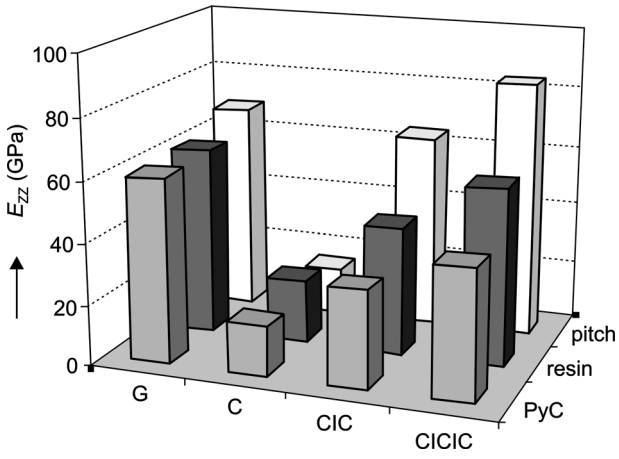


Figure 6. Development of longitudinal modulus E_{zz} at various manufacture levels for the shell specimens A2, B2 a C2.

almost fixed mass increments of about 0.5 g per single impregnation & recarbonisation step (initial mass of the carbonised shells ranged 8.5 – 9.1 g).

The sharp decrease of E_{zz} after the first carbonisation (level *C* in figure 6) is caused by the already mentioned mass-loss of the matrix during its pyrolysis. The decrease of $E_{\phi\phi}$ was so large that its value

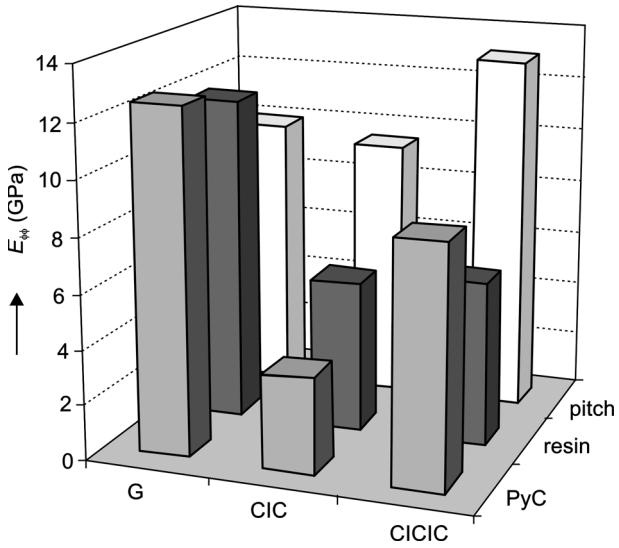


Figure 7. Development of tangential modulus $E_{\phi\phi}$ at various manufacture levels for the shell specimens A2, B2 a C2.

in the *C* level could not ever be detected (figure 7). In spite of the mutual similarity of mass increments and porosity variation for all investigated impregnants the measured development of elastic constants varies with the type of secondary carbon matrix (figure 6 and figure 7). It is the distribution of occurrence (influenced, e.g., by viscosity of the liquid precursor) and microstructure (controlled by its nature) of the secondary carbon matrix which play a key role in the elastic response of the densified CFRC shells. Indeed, we have detected remarkable differences in void filling level even at roughly the same weight increment after densification with either pyrolytic carbon, resin, or pitch.

Pyrolytic carbon is deposited in a very thin layer along surfaces of both inter-bundle (figure 8*a*) and intra-bundle (figure 8*b*) voids. Due to its high anisotropy the layer is clearly seen (as a brighter phase) in partially crossed polarises. Though a substantial filling of narrow voids takes place (figure 9*a*) the major voids remain virtually unfilled (figure 9*b*). The latter

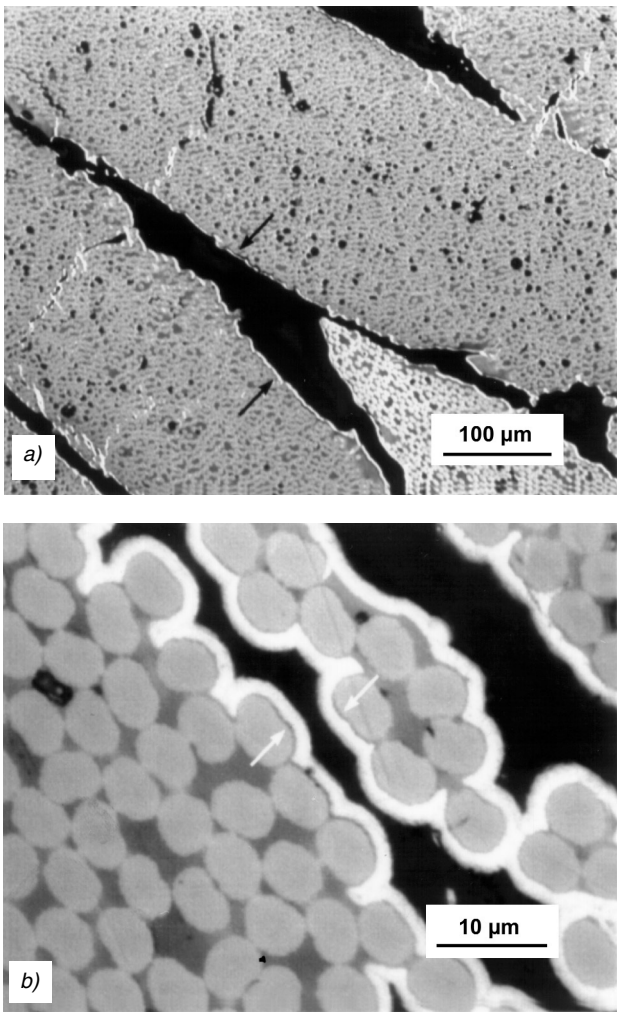


Figure 8. Pyrolytic carbon deposited in a thin layer along surfaces of: *a)* inter-bundle voids, *b)* intra-bundle voids.

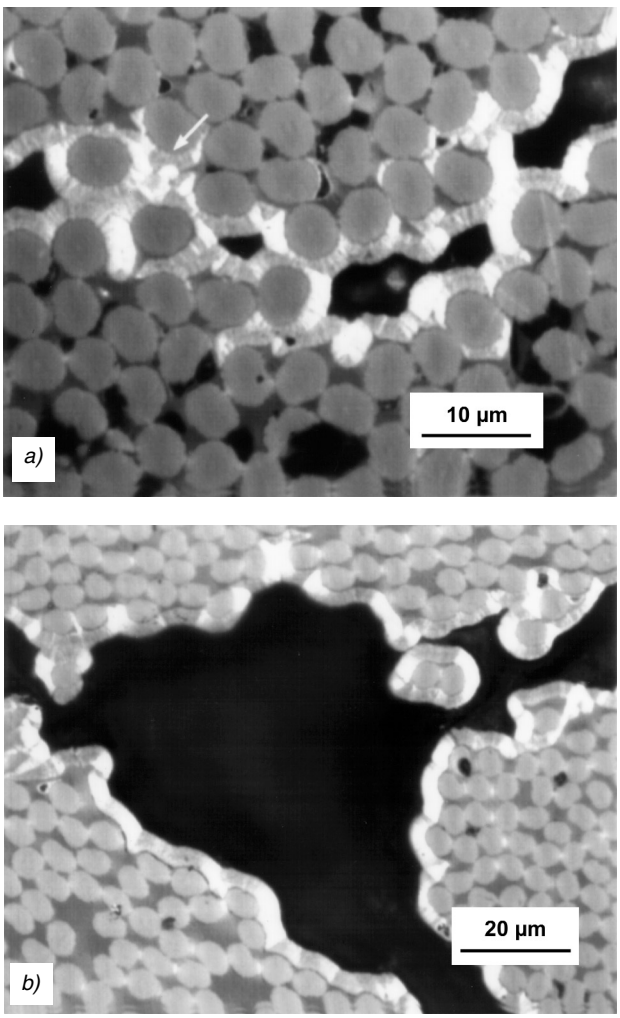
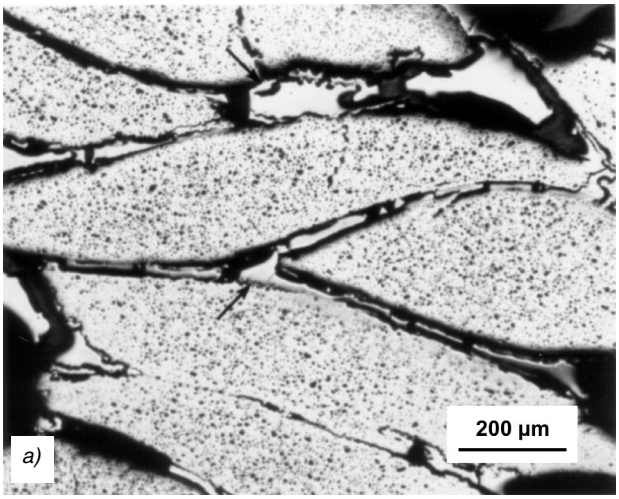


Figure 9. Filling of voids by a pyrolytic carbon layer: *a)* filled narrow voids, *b)* unfilled major voids.



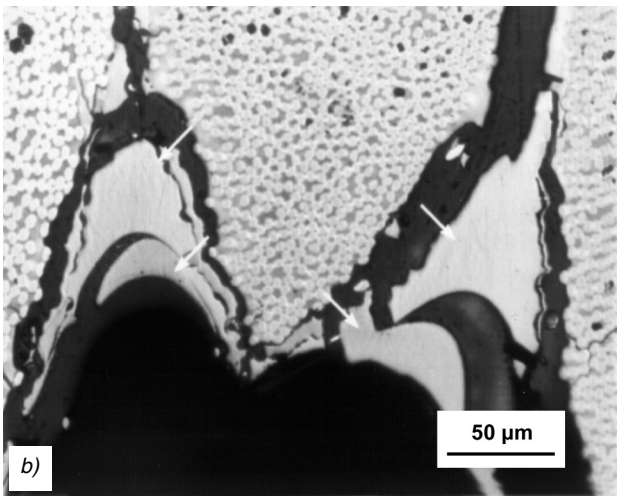
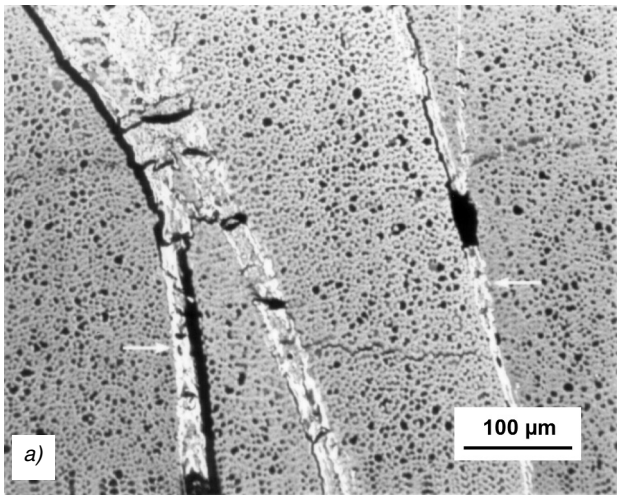


Figure 10. Filling of voids by a carbonised ex-resin matrix: *a)* massive filling of inter-bundle voids, *b)* two subsequent generations of secondary matrix filling a "pocket".



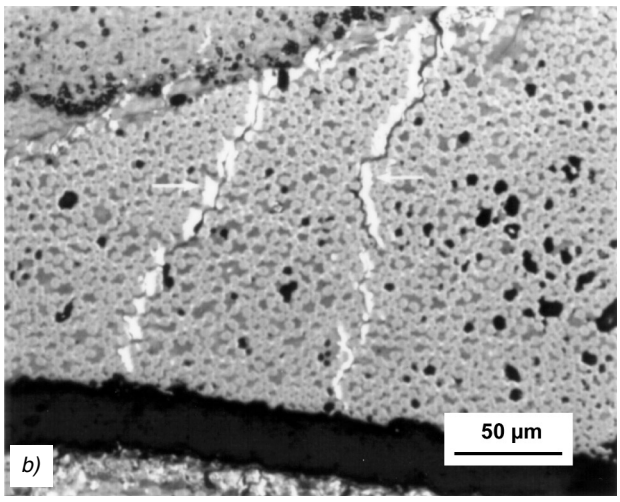


Figure 11. Ex-pitch carbon matrix filling: *a)* inter-bundle voids, *b)* intra-bundle voids.

may be the main reason for relatively low influence of densification with pyrolytic carbon upon elastic moduli – if compared with resin or pitch impregnation (figures 6 and 7).

Carbonised resin ("glass-like" carbon) is isotropic and therefore optically inactive. Nevertheless, massive filling of inter-bundle voids can clearly be seen (figure 10*a*). Moreover, a low viscosity of the molten impregnating resin leads to preferred formation of matrix "pockets" where two subsequent generations of secondary matrix can be distinguished (figure 10*b*).

The molten pitch fills at impregnation both inter-bundle voids (figure 11*a*) and intra-bundle cracks (figure 11*b*). The carbonised pitch is anisotropic and it forms large domains (figure 12) of preferred orientation of graphene layers (i.e., 2-dimensional clusters of basal planes of a nearly graphitic carbon structure). Such an arrangement reveals (due to strong covalent in-plane bonding) a very high Young's modulus along the graphene layer [5].

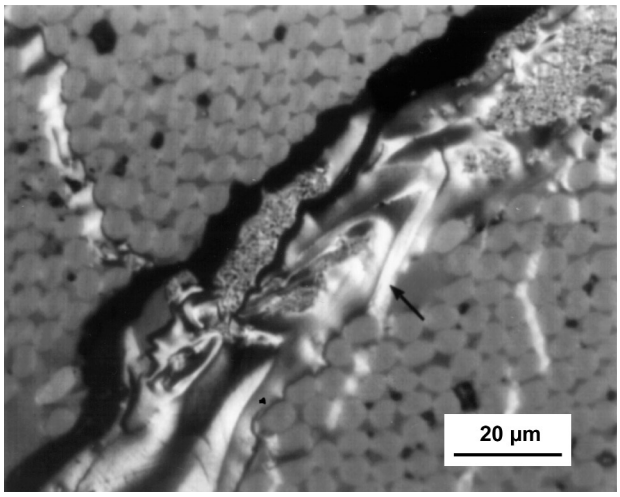


Figure 12. A large domain of anisotropic pitch-based carbon matrix with preferred orientation of graphene layers.

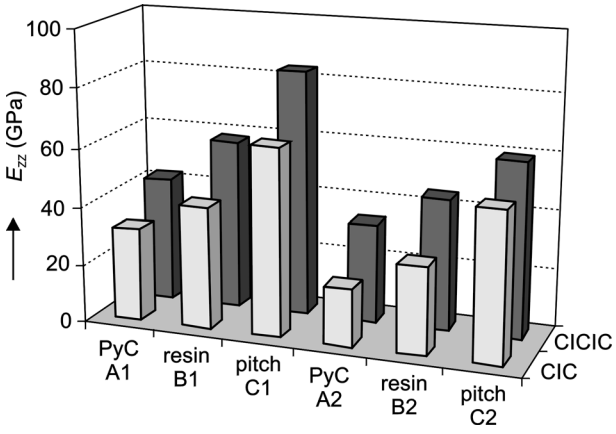


Figure 13. Longitudinal modulus of shells with various secondary matrices and different braiding angles of the reinforcement.

Therefore, densification by pitch impregnation can lead to higher values of elastic moduli than that by resin (figures 6 and 7) even at mutually comparable levels of void volume reduction (figure 5).

The pattern of results on elastic moduli is common for the shells made of the both employed braid types ($\theta = 42°$ and 55°) and confirms the expected influence of the braiding angle θ upon longitudinal modulus E_{zz}, (i.e., higher modulus at lower θ, figure 13).

CONCLUSIONS

Microstructure and elastic properties of carbon--carbon composite shells manufactured using a braided reinforcement can be to considerable extent controlled by their densification. In this process, various types of secondary carbon matrix (pyrolytic carbon, glass-like carbon, or carbonised coal tar pitch) are differently effective in increasing longitudinal and tangential elastic moduli of the shells. In this way, certain degree of freedom is available when controlling the shell's open porosity by impregnation with liquid precursors of secondary carbon matrix or with pyrolytic carbon.

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VLIV IMPREGNACE NA STRUKTURU A ELASTICKÉ VLASTNOSTI SKOŘEPIN Z KOMPOZITU UHLÍK-UHLÍK

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Válcové skořepiny z kompozitu uhlík-uhlík byly připraveny karbonizací tzv. "zelených" kompozitních skořepin vyztužených uhlíkovou splétanou výztuží a nasycených fenolickou pryskyřicí. Takto získaný porézní kompozitní materiál byl zhutňován impregnací různými prekurzory sekundární uhlíkové matrice. Postupný vzrůst tuhosti skořepin byl dokumentován měřením podélného a tečného modulu pružnosti metodou rezonančních frekvencí. V práci je diskutován vliv úhlu spletení výztuže a procesních parametrů (tepelné zpracování, zhutňování a druh impregnantu) na vývoj tuhosti kompozitní skořepiny.